

## Modeling Trichloroethylene Adsorption by Activated Carbon Preloaded with Natural Dissolved Organic Matter Using a Modified IAST Approach<sup>†</sup>

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A model was developed, using an approach based on the Ideal Adsorbed Solution Theory (IAST), to predict trichloroethylene (TCE) adsorption by granular activated carbon (GAC) preloaded with natural dissolved organic matter (DOM) isolated from three surface water sources. The IAST model was formulated for a bi-solute system in which TCE and DOM single-solute uptakes were described by the Langmuir–Freundlich and Freundlich isotherms, respectively. The effect of DOM molecular size and polarity (as measured by XAD 8 resin fractionation) on TCE uptake by preloaded GAC was assessed to identify a reactive fraction of natural water DOM for the purpose of modeling competitive adsorption. Consistent with previous work that identified low molecular weight species as the most reactive with regard to preloading effects (i.e., reducing target compound uptake), the low molecular weight components of the polar (hydrophilic) and nonpolar (hydrophobic) DOM fractions, isolated using ultrafiltration (1 kDa molecular weight cutoff membrane), exhibited significant competitive effects. Furthermore, the effects of these fractions on TCE uptake were similar; therefore, they were considered together to represent a single “reactive fraction” of DOM. On the basis of this finding, isotherms for the <1 kDa low molecular weight DOM fraction of the whole water were measured, and molar concentrations were computed based on an average molecular weight determined using size-exclusion chromatography. The IAST model was modified to incorporate surface area reduction due to pore blockage by DOM and to reflect the hypothesis that TCE molecules can access adsorption sites which humic molecules cannot, thus preventing competition on these sites. The model was calibrated with data for TCE uptake by carbon preloaded with the <1 kDa low molecular weight DOM fraction and was verified by predicting TCE uptake by carbon preloaded with whole natural waters for both constant GAC dose (hence constant DOM loading) and variable GAC dose (hence variable DOM loading) TCE isotherms. Preloading by DOM reduced volume in GAC pores having widths smaller than 1.25 nm (likely accessible

only to TCE) to a greater extent than total pore volume, suggesting preferential blockage of micropores. Such preferential pore blockage may explain, in part, why increased DOM loading decreases the fraction of the total surface area on which no competition between TCE and DOM occurs.

### Introduction

Granular activated carbon (GAC) adsorption has been identified by the Safe Drinking Water Act Amendments of 1986 as the best available technology for removing synthetic organic contaminants (SOCs) from potable water supplies (1). GAC also effectively adsorbs natural dissolved organic matter (DOM), which can significantly reduce the efficiency of activated carbon adsorbers to remove targeted SOCs. This reduction is exacerbated in fixed-bed adsorbers because the mass transfer zone of slower adsorbing DOM components often moves more rapidly than that of many SOCs; therefore, the bed becomes fouled or preloaded ahead of the target SOC. Preloaded DOM is not displaced by most SOCs and can significantly reduce the capacity of granular activated carbon fixed-bed adsorbers for them (2–6). Such reductions have been shown to depend on DOM loading and/or contact time (4–6); therefore, models that incorporate the effects of preloading must account for changes in the competitive effects of DOM with loading.

To predict SOC uptake by preloaded GAC, a competitive sorption model is required; therefore, it is necessary to represent both SOC and DOM sorption properties mathematically. The inherent heterogeneity of DOM (molecular size and chemical structure) requires that such properties be greatly simplified. A widely adopted approach involves an empirical representation of DOM as one or more uncharacterized background components (7–9). The adsorptive properties of such components are determined by comparing single-solute SOC adsorption with adsorption from a solution containing natural organic matter. Adsorptive properties (expressed in terms of model parameters) are then estimated through a statistical optimization using a competitive adsorption model, most commonly the Ideal Adsorbed Solution Theory (IAST) or derivative thereof. In many cases, such models have accurately described SOC adsorption from solutions containing DOM. However, a number of fitting parameters, which may not be unique and which may lack physical significance, must be calculated.

An alternative approach, based on a special simplified case of the IAST called the Simplified Competitive Adsorption Model (SCAM) (10), has been developed (2, 11). The modified SCAM, now termed MSCAM, modeled DOM as a single component for which Freundlich isotherm parameters were measured. In addition, the model incorporates the hypothesis that not all adsorption sites are available to either the target solute or the DOM and employs two fitting parameters to represent the fraction of the total capacity of each solute available for competitive adsorption. The model using three fitting parameters in total (including the DOM molecular weight) accurately described competitive adsorption equilibria between natural surface water DOM and 1,1,2-trichloroethane (10). However, the fitted DOM molecular weights were significantly lower than those commonly reported for natural waters (12–15). Furthermore, the fitting parameters representing the fraction of competitive capacity available for each solute are treated as constant and thus do not take into account changes in the DOM mass loading.

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To overcome some of these limitations, a competitive adsorption model, based on modifications to the IAST, was developed to provide a predictive approach that could be applied to simultaneous and preloading conditions (16). TCE uptake by GAC preloaded with DOM was modeled as a bi-solute system. Competition from whole DOM was represented by a single low molecular weight reactive fraction, based on previous research showing that such components are adsorbed preferentially by microporous activated carbon (17) and are thought to be most reactive in competing with low molecular weight target compounds (11, 18–23). The adsorption isotherm and average molecular weight of this reactive fraction were measured experimentally, avoiding the uncertainty introduced when such properties are employed as fitting parameters.

The IAST model, which accounts for direct site competition assuming that all sites are available to all components in a mixture, was modified to reflect two preloading mechanisms, direct competition for high energy sites and overall capacity reduction due to pore blockage, first proposed by Carter et al. (4, 5) and later verified theoretically and experimentally (24–26). The possibility that some humic molecules are too large (12) to access GAC micropores was addressed by modeling TCE uptake as the sum of competitive uptake by surfaces accessible to DOM molecules and uptake by surfaces inaccessible to DOM, on which there are no competitive effects. The fraction of surface area on which TCE adsorbs without competition ( $\theta$ ) was correlated as a function of reactive DOM loading, an approach consistent with previous studies showing that preloading impacts increase with DOM loading (19, 27). The ability of DOM to adsorb at pore entrances and block access to surface area, rendering it unavailable for TCE adsorption, was accounted for by measuring the reduction in surface area that resulted from preloading, an approach consistent with other studies reported in the literature (18, 28). Using single-solute isotherm parameters and  $\theta$ -values calibrated as a function of reactive fraction loading, modified IAST (MIAST) *predictions* for TCE adsorption by carbon preloaded with *whole* humic acid solutions over a wide range of loadings (ranging from 12 to 87 mg/g) were calculated (16).

While the MIAST modeling approach provided accurate predictions based on a mechanistic understanding of DOM preloading mechanisms, it was developed using a soil-derived humic acid (16). It is known that the composition of aquatic and soil DOM is different, both in terms of molecular weight distribution and chemical functionality that may affect DOM affinity for the carbon surface. Therefore, one objective of this work was to further develop and verify the model for predicting TCE uptake by GAC preloaded with natural water DOM. Model verification included assessing the ability to predict both constant GAC dose (hence constant DOM loading) and variable GAC dose (hence variable DOM loading) TCE isotherms. A second objective was to provide a basis for interpreting the effects of loading on the surface area inaccessible to DOM on which TCE adsorbs without competition. To this end, a detailed analysis of GAC pore volume changes upon preloading was performed.

## Methods and Materials

**Solutes.** Deionized (DI) water was prepared by filtering municipal tap water sequentially through an activated carbon bed, a mixed anion/cation exchange bed, and a 0.2  $\mu\text{m}$  PTFE microfilter. Reagent-grade I water (MQ water) was prepared by filtering DI water using a Milli-Q system (Millipore, Bedford, MA). DOM was isolated from the Intercoastal Waterway, Myrtle Beach, SC (MB); the Edisto River, Charleston, SC (CH); and the Tomhanock Reservoir (TMK) in Rensselaer County, NY, employing a field-operated reverse osmosis unit as described previously (29). These three

freshwaters, which represent diverse geographic origin and a wide range of bulk properties, are all municipal drinking water sources. The whole DOM (WH) matrix was subsequently separated into operationally defined nonpolar, hydrophobic (HPO) and polar, hydrophilic (HPL) fractions using techniques based on minor modifications to the methods developed by researchers at the USGS (30, 31) as described previously (29). Low molecular weight components of the whole DOM (WH) matrix and the HPL and HPO fractions were isolated using a 1 kDa molecular weight cutoff (MWCO) hollow-fiber ultrafiltration (UF) membrane as described previously (29).

**GAC.** Calgon TOG 20x50 (TOG) activated carbon was used for all adsorption work in this phase. TOG is a bituminous coal-based, low water-soluble ash (<1%, manufacturer data), steam-activated carbon designed specifically for drinking water filter units with short contact times. Except for the smaller particle size and slightly lower surface area (922  $\text{m}^2/\text{g}$ ), TOG carbon is expected to behave comparably to Calgon F400 GAC in capacity/isotherm applications, allowing for comparative analysis with other studies using this adsorbent (personal correspondence, Andy McClure, Calgon Corp.). As-received carbon was sequentially batch-rinsed, decanted, and then boiled in MQ water for 30 min. Carbon was subsequently dried to constant mass at 105  $^{\circ}\text{C}$  and stored in a vacuum desiccator until use.

Surface area and pore volume distribution characterization of the TOG carbon, both as-received and following preloading by DOM, were based on analysis of nitrogen isotherm data measured at 77 K with a gas adsorption analyzer (Autodorb 1-C, Quantachrome Corp., Boyton Beach, FL). Each isotherm consisted of 55 data points, and isotherms were measured over the pressure range of  $p/p_0 \sim 10^{-5}$  to 0.995. Both as-received and carbons preloaded with the DOM were dried to constant weight at room temperature in a vacuum desiccator and were subsequently outgassed for at least 24 h in a vacuum oven at 60  $^{\circ}\text{C}$  followed by at least 8 h outgas at very low pressure and 105  $^{\circ}\text{C}$ . Outgas temperatures were maintained at these relatively low values to minimize changes in adsorbed DOM structure. All calculations were performed using the software included with the instrument package. Total surface area was determined by fitting the Brunauer, Emmett, and Teller (BET) adsorption isotherm equation to at least 10 low-pressure isotherm points ( $p/p_0 \sim 0.01$ –0.1). Pore volume and surface area distributions were also calculated using Density Functional Theory (DFT).

**TCE Uptake by As-Received Carbon.** TCE uptake by as-received carbon was measured by equilibrating GAC (0.06–0.18 g of GAC/L) with TCE solutions (initial concentrations ranged from 0.08 to 206.8 mg/L) in headspace-free 250-mL amber-colored batch reactors (glass bottles) sealed with screw caps and Teflon-lined silicone septa or 60-mL vials with Teflon-lined silicone septa and aluminum crimp seals for 2 weeks in the dark at room temperature. Reactors were kept mixed via continuous end-over-end tumbling. Equilibrium TCE concentration was determined using liquid extraction (into hexane) by gas chromatography with electron capture detection calibrated using external standards prepared the same as samples. Control reactors confirmed that changes in TCE concentration due to factors other than uptake by GAC were negligible.

**DOM Preloading.** DOM stock solutions stored at pH 4 were diluted if necessary, and adjusted to neutral pH prior to filtration using a 0.45- $\mu\text{m}$  hydrophilic poly(ethersulfone) membrane (Supor, Gelman Sciences, Ann Arbor, MI). All DOM solutions were amended with 100 mg/L sodium azide to limit microbial activity and 0.001 M phosphate buffer to maintain constant pH  $7 \pm 0.2$ . Solution pH adjustments were made using HCl or NaOH as needed. Ionic strength was

adjusted to 0.01 M as NaCl by either salt addition or dilution as needed. MQ water amended with sodium azide, phosphate buffer, and NaCl was used for all dilutions to maintain constant background ion concentrations.

GAC (0.06–0.25 g/L of DOM solution) was preloaded under oxic conditions in completely mixed 250-mL amber glass batch reactors (sealed with screw caps and Teflon-faced silicon septa) for 30 d. Initial DOM concentrations ranged from 3 to 16.9 mg of DOC/L. Following the 30-d DOM contact time, aqueous-phase DOC was measured to determine DOM loading. Then, a series of reactors containing the same preloaded GAC mass were subsequently spiked with a methanol solution of TCE to attain initial TCE concentrations ranging from 75 to 15 000  $\mu\text{g/L}$ , keeping the methanol concentration less than 0.001 mol fraction, at which concentration no cosolvent effects are expected (4). This approach ensures that all competition was from preadsorbed organic matter. Unless otherwise noted, TCE isotherms employed a constant GAC dosage to keep the DOM loading constant. Reactors were filled completely, sealed with no headspace, and kept well-mixed via end-over-end tumbling for a period of 2 weeks. Rate studies have shown that this time is sufficient to reach equilibrium for a similar GAC with larger particle size (4).

**Isotherm Models.** The bottle point method used in this research leads to adsorption isotherms where each point on the isotherm corresponds to an individual completely mixed batch reactor. For each isotherm point, solute partitioning to the solid phase ( $q_e$ ) is determined on a mass solute per mass adsorbent basis, by a mass balance calculation on the liquid phase. Surface water DOM contained a significant nonadsorbable fraction, in contrast to the low molecular weight fraction of the soil humic substances studied previously. This was incorporated into the DOM isotherm to express uptake in terms of adsorbing components using a modified Freundlich isotherm model:

$$q_e = K_F(C_e - C_{\text{non}})^n \quad (1)$$

where  $C_e$  is the equilibrium liquid-phase concentration,  $K_F$  is a unit capacity factor,  $n$  is a measure of sorption intensity or heterogeneity, and  $C_{\text{non}}$  is the nonadsorbing fraction, estimated experimentally from the residual liquid-phase concentration in the high adsorbent dose region of the DOC isotherm. Single-solute TCE uptake was described using the three-parameter Langmuir–Freundlich (LF) model:

$$q_e = \frac{Q^o(bC_e)^n}{1 + (bC_e)^n} \quad (2)$$

where  $Q^o$  is the sorbent capacity,  $b$  is an average site energy, and  $n$  is a measure of the site energy distribution. Excellent fits of TCE uptake by preloaded carbon, providing accurate predictions of uptake at specified values of  $C_e$  necessary for comparative analysis, were obtained using the Dubinin–Astakhov (DA) isotherm model:

$$q_e = Q^o \exp\left[\frac{-(RT \ln(C_{\text{sat}}/C_e))^n}{B}\right] \quad (3)$$

where  $Q^o$  is interpreted as a micropore capacity,  $C_{\text{sat}}$  is the TCE solubility (taken as 1100 mg/L),  $n$  is a parameter related to the adsorbent pore structure, and  $B$  is an energy parameter. This was employed as a two-parameter model using an average value of  $n = 1.879$ .

Two-parameter isotherm model parameters and their statistics were calculated using the regression analysis tool incorporated in a commercial spreadsheet software program (Microsoft Excel 97). Nonlinear and three-parameter isotherm

model parameters and their statistics were calculated using the pre-commercial V2 Beta 15, 32 bit version of Kypplot as written by Koichi Yoshioka.

## Theory

The total solid-phase TCE uptake ( $q_e$ ) and capacity ( $Q^o$ ) are the sum of uptake and capacity by competitive and non-competitive surfaces:

$$q_{e,\text{total}} = q_{e,\text{comp}} + q_{e,\text{non-comp}} \quad (4)$$

$$Q_{\text{total}}^o = Q_{\text{comp}}^o + Q_{\text{non-comp}}^o \quad (5)$$

Defining a fraction of the surface area on which TCE adsorbs without competition is equivalent to defining a fraction of the capacity  $\theta Q^o$  that can be occupied with no competition. Therefore

$$Q_{\text{total}}^o = (1 - \theta)Q^o + \theta Q^o \quad (6)$$

The uptake of TCE by surfaces without competition is calculated from the LF single-solute isotherm equation modified by  $\theta$ :

$$q_{\text{TCE,non-comp}} = \frac{\theta Q^o(bC_e)^n}{1 + (bC_e)^n} \quad (7)$$

Therefore, the total TCE uptake is

$$q_{\text{TCE,TOTAL}} = \frac{\theta Q^o(bC_e)^n}{1 + (bC_e)^n} + q_{\text{TCE,IAST}} \quad (8)$$

Only the surface area available to both TCE and DOM is included in the IAST calculations; therefore, the TCE single-solute isotherm used to compute  $q_{\text{TCE,IAST}}$  to provide model input for these calculations is,

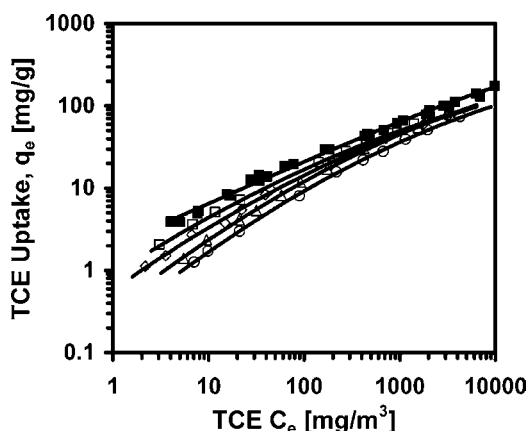
$$q_{\text{TCE,IAST}} = \frac{(1 - \theta)Q^o(bC_e)^n}{1 + (bC_e)^n} \quad (9)$$

and the initial concentration of TCE used as input to the IAST calculations is adjusted by subtracting the mass of TCE adsorbed by surfaces without competition from the total  $C_o$ . Details of the IAST modeling approach have been presented previously (16); model equations are tabulated in the Supporting Information. All model calculations were performed using an optimization scheme based on a generalized reduced gradient (GRG) nonlinear programming algorithm implemented in a commercial software package (Microsoft Excel).

## Results and Discussion

**Reactive Fraction of Natural Water DOM.** For all three whole DOMs, it was found that TCE uptake was diminished on the preloaded carbon relative to uptake in the TCE single-solute system, as expected. Furthermore, as shown by the data and DA isotherm model fits (solid lines) in Figure 1, the capacity reduction was greatest at higher DOC loadings and the percent reduction was most significant at low TCE residual concentrations, consistent with previous reports (4, 24, 25). The effect of DOM molecular weight and hydrophobic character (as measured by XAD resin fractionation) on TCE uptake by preloaded AC was assessed to identify a reactive fraction of natural water DOM (components responsible for reduction in TCE uptake) for the purpose of modeling competitive adsorption as described above.





**FIGURE 1.** Effect of TMK whole NOM loading on TCE uptake by preloaded TOG carbon. Filled squares are single solute TCE uptake with Langmuir–Freundlich model fit (line). Open symbols are TCE uptake by preloaded carbon fitted by the Dubinin–Ashtakov isotherm model (lines); open squares = 18.3 mg/g; open diamonds = 25.0 mg/g; open triangles = 30.8 mg/g; open circles = 37.7 mg/g.

In previous work, Newcombe et al. (18) found that DOM components passing a 500 Da UF membrane and subsequently isolated by adsorption to XAD-8 resin at pH 1 exerted stronger competition with 2-methylisoborneol than larger molecular size fractions. Kilduff et al. (19) found that DOM competition with TCE was primarily due to a low molecular weight reactive fraction (defined operationally as the fraction of humic acid passing a nominal 3 kDa MWCO UF membrane) having weight-averaged molecular weight of 1400 g/mol (as PSS). Newcombe et al. (22) concluded that NOM components having molecular weight less than about 600 Da were the major contributors to competition with 2-methylisoborneol. Li et al. (23) showed that NOM molecules with molecular weights between 200 and 700 Da appeared to be responsible for competition with atrazine. On the basis of this research, we evaluated whether the components passing a 1 kDa MWCO UF membrane could alone be considered the reactive fraction of the waters studied here. As shown in Table 1, molecular weights (weight-averaged) of this fraction were 646, 731, and 717 Da for the TMK, MB, and CH waters, respectively. Therefore, the molecular weight of our <1 kDa fraction is consistent with the molecular weights of reactive DOM components identified in the literature. In addition, preparative-scale UF membranes are available to prepare this size fraction. As will be shown, this new definition of the reactive fraction produced quite satisfactory results; it was not necessary to consider higher MW components.

The ability of the low molecular weight fraction to account for the reactivity of the whole water was assessed by comparing TCE uptake by GAC preloaded with whole water and with the <1 kDa UF fraction, as a function of the <1 kDa fraction loading. The <1 kDa fraction loading from the whole water was computed assuming that this fraction adsorbs preferentially from the original mixture, as shown previously (17).

As shown in Figure 2, TCE uptake by GAC preloaded with whole water and with the <1 kDa UF fraction, computed for three TCE equilibrium concentrations ( $C_e = 10, 100, \text{ and } 1000 \text{ mg/m}^3$ ) using DA model fits, was similar over a wide range of <1 kDa DOM loading. Remarkably, the impact of preloading (when expressed in terms of the reactive fraction loading) was quite similar for the three different surface waters. These data and analyses confirm that the reactivity of the three whole waters evaluated in this research can be attributed to the <1 kDa fraction.

It is known that surface waters contain both hydrophobic and hydrophilic components. Because carbon surfaces are

predominantly hydrophobic, we hypothesized that only the hydrophobic fraction of the <1 kDa low molecular weight fraction of the whole water was reactive in reducing TCE uptake and could therefore be treated as a single reactive component. To assess the validity of this hypothesis, the <1 kDa components of the polar (hydrophilic, HPL) and nonpolar (hydrophobic, HPO) fractions of each water, as defined operationally based on preferential binding to XAD (methyl methacrylate) resin at pH 2, were isolated. Polar and nonpolar composition of surface waters is tabulated in Table 1. TCE uptake by GAC preloaded with these fractions is shown in Figure 3. The impact of preloading for the HPL <1 kDa fraction and the HPO <1 kDa fraction is surprisingly similar for comparable loadings; this was observed for the other two surface waters as well (data not shown). These results reject the hypothesis that the hydrophobic fraction of the <1 kDa low molecular weight fraction of the whole water was solely reactive in reducing TCE uptake; rather, the nonhumic HPL fraction of these surface waters plays an important role in competitive adsorption phenomena, at least for the TOG carbon studied here. Therefore, it is imperative to include both the HPO and HPL low molecular weight fractions in any competitive sorption model. However, because they are similarly reactive, treating the <1 kDa fraction as a single reactive fraction appears justified for these waters. Therefore, subsequent experiments employed the <1 kDa fraction of whole DOM without fractionation by polarity.

While MW is an important DOM property in the context of competition with TCE, it is possible that other chemical properties of the low MW components contribute to their reactivity. However, among the properties measured in this work (polarity, specific UV absorbance, and acidity, tabulated in Table 1), MW appears to best predict the reactivity of the <1 kDa components. Whereas it might be expected that aromatic species could compete well with TCE, the aromaticity of the <1 kDa components, as measured by specific UV absorbance (SUVA), is lower than the whole water. It might also be expected that species having high acidity would exhibit lower aqueous solution-phase fugacity and lower affinity for the relatively hydrophobic GAC surface, yet the acidity of the <1 kDa fraction is higher than that of the whole waters.

The <1 kDa DOM fraction isotherm data and best-fit Freundlich isotherms are shown in Figure 4. The DOM  $C_e$  values were corrected for the concentration of nonadsorbing DOM components, measured as the DOM concentration remaining at very high sorbent dosages (not shown), because nonadsorbable components cannot compete with TCE. The TCE isotherm, fitted with the LF model for purposes of IAST modeling, is shown in Figure 4 (in molar units) for comparison. TOG capacity for TCE was estimated as 5.1 mmol/g assuming complete monolayer coverage using the BET surface area of 922 m<sup>2</sup>/g and a circular projected area (approximated from the three-dimensional van der Waals surface area of TCE) of  $3.0 \times 10^{-19} \text{ m}^2/\text{molecule}$  (32). Therefore, the best-fit LF  $Q^0$  value of 599 mg/g represents about 89% of total BET surface area coverage.

**Surface Area Reduction.** It was previously shown that pore blockage by preloaded DOM can reduce the effective surface area available to TCE (4, 16, 24, 25). Assuming the energetic character of the inaccessible surface area is representative of the GAC overall, this capacity reduction can be expressed in terms of a reduction in the single-solute LF capacity parameter,  $Q^0$ . BET surface area (SA) was measured for carbons preloaded with various <1 kDa DOM loadings and compared to that measured for nonpreloaded carbon ( $SA_0$ ). The effective surface area remaining after preloading ( $SA/SA_0$ ) was then correlated to <1 kDa DOM loading as shown in Figure 5 for the three waters studied. As

TABLE 1. DOM Characterization

	TMK			MB			CH		
	WH	HPO	HPL	WH	HPO	HPL	WH	HPO	HPL
Raw Water									
DOC <sup>a</sup>	3.59			23.82			3.44		
SUVA $\lambda = 254 \text{ nm}^b$	2.08	2.92	1.54	4.40	4.95	3.02	4.70	5.54	3.06
SUVA $\lambda = 280 \text{ nm}^b$	1.32	1.31	1.0	3.30			3.53		
% HPO	36.4			65.9			60.8		
% HPL	63.6			34.1			39.2		
$M_w^c$	1294	1028	1724	3372	1797	3473	6548	2204	4184
$M_n^c$	515	546	600	1049	1243	900	998	991	847
% <1 kDa	56.4			38.3			32.7		
acidity (pH 3) <sup>d</sup>	11.2	10.6	12.4	8.6	7.8	11.6	8.2	5.0	12.4
acidity (pH 10) <sup>d</sup>	17.6	2.0	24.6	5.7	6.1	14.5	16.3	5.1	45.0
<1 kDa Fraction									
$M_w^c$	646	404	670	731	594	599	717	650	766
$M_n^c$	407	276	465	449	431	446	468	441	480
SUVA $\lambda = 280 \text{ nm}^b$	1.31	1.99	.97	1.66	2.29	1.62	1.85	2.34	1.82
acidity (pH 3) <sup>d</sup>	14.7			10.6			17.6		
acidity (pH 10) <sup>d</sup>	40.9			13.2			78.1		

<sup>a</sup> Nonpurgeable DOC (mg/L) determined by high-temperature wet oxidation (O.I. Analytical, College Station, TX) calibrated using external potassium hydrogen phthalate standards. <sup>b</sup> SUVA ( $\text{L mg}^{-1} \text{ m}^{-1}$ ) calculated from DOC measurement and absorbance measurement made using a 1-cm quartz cell and a Hewlett-Packard HP 8452A diode array spectrophotometer with a wavelength accuracy of 2 nm, a wavelength reproducibility of 0.05 nm, a spectral bandwidth of 2 nm, a stability of <0.001 AU, and a baseline noise of <0.0003 AU rms. <sup>c</sup> Weight- ( $M_w$ ) and number- ( $M_n$ ) averaged molecular weights (g of PSS/mol) measured using a Waters Protein Pak 125 column (silica-based gel stationary phase; size exclusion limits of 1000–80,000 MW) and an HP 1100 HPLC system (25 °C, 0.75 mL/min, injection volume of 100  $\mu\text{L}$ , mobile phase ionic strength 0.1 M as NaCl, pH 6.8,  $\text{PO}_4$  buffer) calibrated with poly(styrene sulfonate) standards (MW 4600, 8000, 18000, and 35000). <sup>d</sup> DOC samples were adjusted to pH 3, purged with  $\text{CO}_2$ -free  $\text{N}_2$  and titrated under positive  $\text{N}_2$  pressure with purified, standardized NaOH titrant solution to the indicated pH. Solution pH was measured using an Orion Ross semi-microcombination epoxy body probe and Accumet model 50 (Fisher Sci) pH meter. Titrant was delivered to the sample using a Class A, 5 mL microburette, marked at 0.01 mL increments. Titrant was renewed daily to minimize effects of atmospheric  $\text{CO}_2$  contamination.

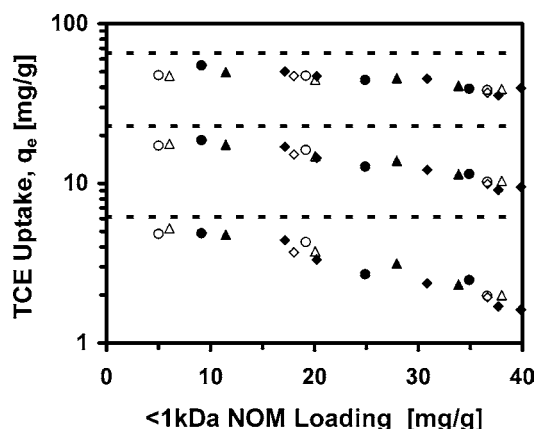


FIGURE 2. TCE uptake by preloaded TOG carbon calculated from Dubinin–Ashtakov fits. Dashed lines represent single solute uptake:  $C_0 = 10 \text{ mg/m}^3$ ,  $q_e = 6.15 \text{ mg/g}$ ;  $C_0 = 100 \text{ mg/m}^3$ ,  $q_e = 22.81 \text{ mg/g}$ ;  $C_0 = 1000 \text{ mg/m}^3$ ,  $q_e = 65.41 \text{ mg/g}$ . Carbon was preloaded with whole NOM (filled symbols) and the <1 kDa fraction isolated by ultrafiltration (open symbols). Uptake is expressed as a function of the <1 kDa fraction loading; loading of this fraction from the whole water was computed assuming that this fraction adsorbs preferentially. Source waters: diamonds = TMK; triangles = MB; circles = CH.

seen by visual inspection of the graphical results and the correlation results, there is a linear relationship between the mass of DOC loaded and the reduction in surface area as measured by BET analysis. In addition, the <1 kDa DOM fraction preloading effect on BET surface area is remarkably similar for the three different waters.

Surface area reduction was accounted for in IAST predictions of TCE uptake by reducing the single solute  $Q^0$  parameter in proportion to the correlated reduction in BET surface area. Such predictions corresponded closely to observed TCE uptake at high concentrations; however, the model overpredicted the competitive effect of the DOM in

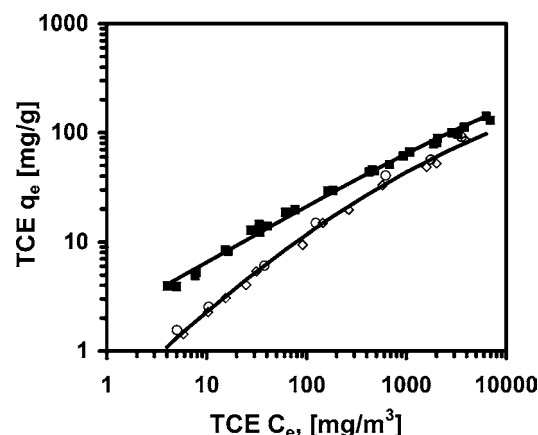


FIGURE 3. Effect of NOM <1 kDa polarity on TCE uptake by preloaded TOG carbon. Filled squares are single solute TCE uptake fitted by the Langmuir–Freundlich isotherm (line). TCE uptake by preloaded TOG carbon shown as open symbols fitted by the Dubinin–Ashtakov isotherm model (line); diamonds = 36.6 mg/g TMK <1 kDa hydrophobic fraction; circles = 32.9 mg/g TMK <1 kDa hydrophilic fraction.

the low concentration range. As outlined above, the MIAST model addresses this through the hypothesis that TCE can access sites that DOM cannot. In the low TCE equilibrium concentration range, a higher percentage of TCE adsorbs in pores that are not accessible to NOM. Because IAST assumes equal access to all sites, the model error is therefore greatest in this range. The MIAST  $\theta$  parameter accounts for this by defining a fraction of the carbon surface on which TCE can adsorb without competition from NOM. This has the effect of increasing the number of high-energy sites available to TCE, thus increasing the uptake in the low concentration region. At higher TCE equilibrium concentrations, the fraction of total TCE uptake in pores not accessible to NOM is smaller, and hence the error in IAST predictions is smaller as well.

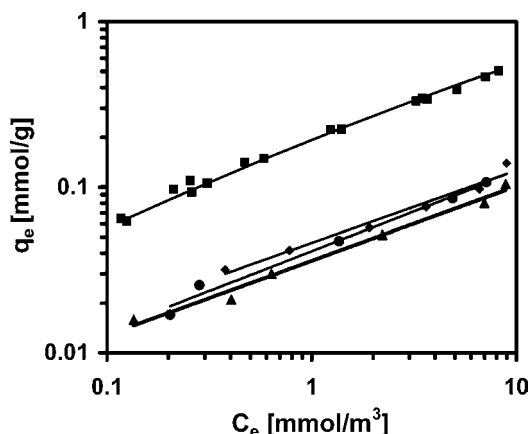


FIGURE 4. Comparison of TCE and <1 kDa NOM uptake by TOG carbon, expressed on a molar basis. Squares are single solute TCE uptake fitted by the Langmuir–Freundlich isotherm model (line); diamonds = TMK <1 kDa fraction uptake fitted by the Freundlich isotherm model (line); triangles = MB <1 kDa fraction uptake fitted by the Freundlich isotherm model (line); circles = CH <1 kDa fraction uptake fitted by the Freundlich isotherm model (line).  $C_e$  values were corrected for the nonadsorbing <1 kDa NOM fraction.

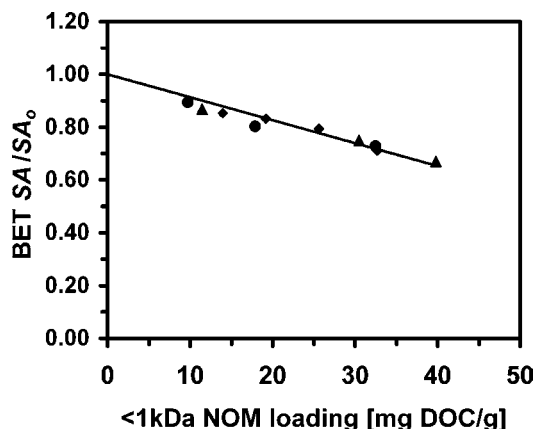


FIGURE 5. Measured reduction in BET surface area after preloading of the <1 kDa fraction. Diamonds = TMK <1 kDa fraction; triangles = MB <1 kDa fraction; circles = CH <1 kDa fraction.

**Model Calibration.** the fraction of sites on which TCE adsorbs without competition ( $\theta$ ) was calibrated using isotherm data for TCE uptake by carbon preloaded with <1 kDa DOM fractions for a range of DOM loadings. Six representative isotherm points spanning the range of measured TCE concentrations were used for calibration. For each point the model-calculated TCE  $q_{\text{total}}$  was compared to the DA isotherm fit to experimentally measured data, at the same value of  $C_e$ . Optimization was achieved by varying  $\theta$  to minimize the sum of the squared residuals (SSR) of log-transformed  $q_{\text{total}}$  values for the chosen points.

Figure 6 illustrates representative MIAST model calibration fits to TCE uptake by TOG preloaded with different amounts of the TMK <1 kDa fraction. Accounting for pore blockage and a noncompetitive surface area provides excellent fits to the data; similar results were found for the MB and CH waters. Consistent with findings for the soil humic acid used to originally develop the MIAST model, it was found that calibrated values of  $\theta$  decreased linearly with increased DOM loading, over the range of loadings studied, as shown in Figure 7. As discussed in the next section, these correlations were used to predict TCE uptake by TOG carbon preloaded with whole natural waters. Potential causes for the observed variation in values will be discussed subsequently.

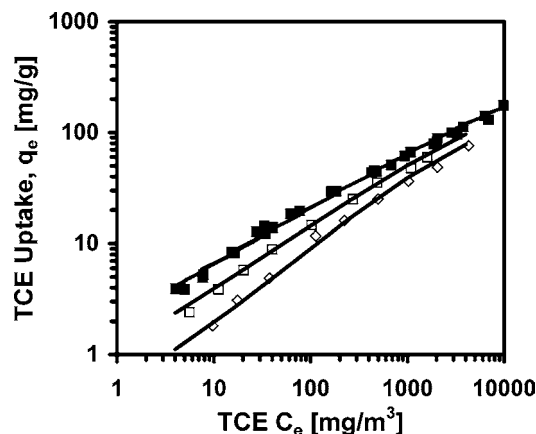


FIGURE 6. MIAST model calibration of theta after correcting for measured surface area reduction. Filled symbols are TCE single solute uptake fitted by the Langmuir–Freundlich isotherm model (line). Open symbols are TCE uptake by <1 kDa TMK fraction with MIAST calibration (lines); squares = 18.0 mg/g loading,  $SA/SA_0 = 0.84$ ,  $\theta = 0.650$ ; diamonds = 36.6 mg/g loading,  $SA/SA_0 = 0.683$ ,  $\theta = 0.331$ .

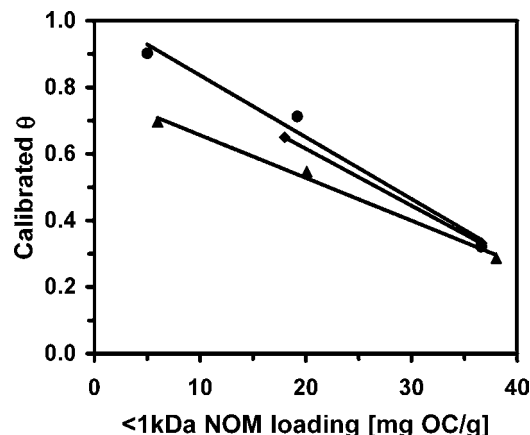
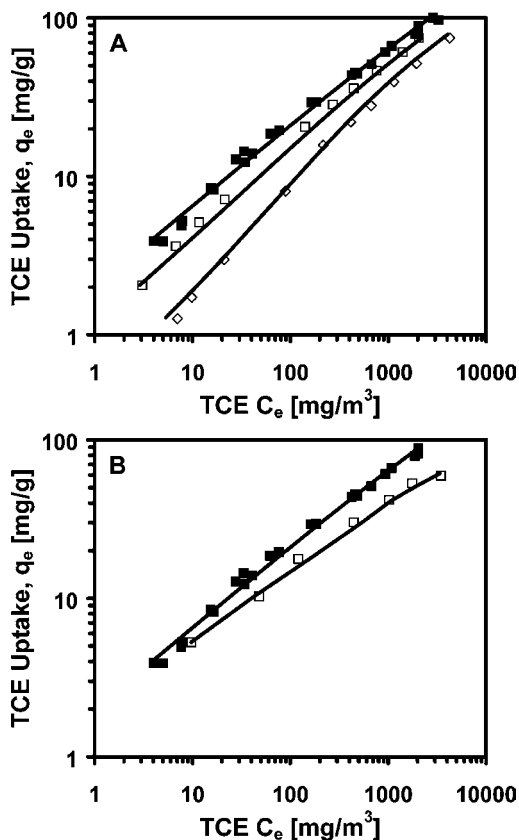


FIGURE 7. Effect of <1 kDa fraction NOM loading on calibrated values of the fraction of sorbent surface area,  $\theta$ , on which TCE adsorbs without competition from NOM. Preloaded <1 kDa fraction: diamonds = TMK; triangles = MB; circles = CH <1 kDa.

**Model Predictions.** MIAST predictions for TCE adsorption by carbon preloaded with whole DOM were calculated using the surface area reduction measured and correlated with <1 kDa loading (Figure 5) and the noncompetitive fraction of the sorbent surface calibrated and correlated with <1 kDa loading (Figure 7).

The initial concentration of reactive (competitive) organic matter in the whole DOM solution was calculated using the <1 kDa DOM fraction contribution to the whole DOM based on ultrafiltration (56%, 38%, and 33% by mass for the TMK, MB, and CH waters, respectively) corrected for the fraction of <1 kDa DOM that was nonadsorbable, estimated from the <1 kDa DOM isotherms. Based on evidence that smaller components are adsorbed preferentially from a whole DOM solution, all of the components loaded from the whole DOM solution are assumed to be from the <1 kDa fraction when the total loading is less than that calculated from the experimentally determined <1 kDa fraction contribution. When the mass of whole DOM preloaded exceeded that which could be attributed to the <1 kDa fraction, the mass of <1 kDa DOM preloaded (as DOC) was calculated assuming that all of the <1 kDa fraction was loaded, and the difference between the total loading and the calculated <1 kDa fraction loading was not considered in model calculations.



**FIGURE 8.** MIAST model predictions of TCE uptake by TOG preloaded with whole TMK water. Filled squares are TCE single solute uptake fitted by the Langmuir–Freundlich isotherm model (line). Open symbols are TCE uptake by carbon preloaded with whole TMK, lines are MIAST predictions. Panel A: Constant dose methodology. Open squares = 18.3 mg/g loading,  $SA/SA_0 = 0.842$ ,  $\theta = 0.667$ ; open diamonds = 37.7 mg/g loading,  $SA/SA_0 = 0.687$ ,  $\theta = 0.315$ . Panel B: Variable dose methodology. Open squares = carbon dose ranged from 0.06 to 1.55 g/L; fraction of noncompetitive surface area,  $\theta$ , ranged from 0.140 to 0.854; surface area reduction,  $SA/SA_0$ , ranged from 0.611 to 0.924.

Representative model predictions for TCE uptake by GAC preloaded with whole TMK DOM (using a constant GAC dose methodology) are illustrated in Figure 8A; similar predictive accuracy was achieved for the three different surface waters, for initial DOC concentrations ranging from 3 to 11.6 mg/L, and adsorbent doses ranging from 0.06 to 0.20 g/L. Additional figures are available in the Supporting Information. The accuracy of the model predictions is excellent over the entire TCE concentration range, verifying the modeling approach for natural surface water DOM.

**Variable Dosage Isotherm Methodology.** Thus far in the development of the MIAST model all competitive isotherm experiments were performed using the constant adsorbent dose bottle point methodology. In contrast, much of batch system DOM competitive adsorption modeling work reported in the literature has been based on variable dose experimental conditions. Furthermore, all DOM single-solute isotherms reported in the literature, either empirically determined or experimentally measured, have been expressed in terms of the Freundlich equation. However, different DOM isotherms may be measured depending on the initial DOC concentration and the isotherm methodology used because DOM occurs as a complex mixture (the components of which have a range of access to, and affinity for, the adsorbent surface), and isotherm data are expressed in terms of organic carbon, a lumped parameter (33, 34). This detail is often not addressed in many literature studies.

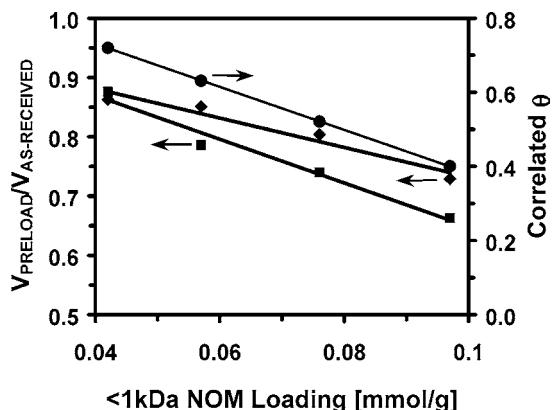
For a single solute, the isotherm shape and position is independent of carbon dosage and initial concentration. A major tenet of the MIAST model is that the  $<1$  kDa fraction can be considered as a “single reactive component”. As a further test of this hypothesis and to evaluate the efficacy of the modeling approach using experimental conditions consistent with other studies, the model was applied to predict TCE uptake by carbon preloaded with TMK DOM using the variable dose methodology. A high initial concentration ( $\sim 17$  mg of DOC/L) of whole TMK water was used to ensure a significant preloading effect. Carbon dosages ranged from 0.06 to 1.55 g/L, and total DOM loading ranged from 9 to 48 mg of DOC/g. The model was applied predictively as described above using the surface area reduction measured and correlated with  $<1$  kDa loading (Figure 5) and the noncompetitive fraction of the sorbent surface calibrated and correlated with  $<1$  kDa loading (Figure 7). However, in contrast to predictions of TCE uptake by preloaded carbon using a constant-dose methodology, when variable dosages are used, the  $<1$  kDa fraction DOM loading and hence model parameters are different for each isotherm point; here the fraction of noncompetitive surface area ( $\theta$ ) ranged from 0.140 to 0.854 and the surface area reduction ( $SA/SA_0$ ) ranged from 0.611 to 0.924. The MIAST prediction, shown in Figure 8B, is quite satisfactory for the range of loadings and TCE residual liquid-phase concentrations encountered. Note that, in contrast to isotherms measured with the constant dose methodology, the largest relative reduction in TCE uptake occurs in the high concentration region. This is because data in this region corresponds to low sorbent dosages and therefore high DOM loadings.

**Non-Competitive Surface Area ( $\theta$ ) Interpretation.** Under the hypothesis that  $\theta$  represents the fraction of the surface area that TCE can access but DOM molecules cannot, one interpretation of the observed decrease in  $\theta$  with increased DOC loading is that DOM molecules are able to access smaller pores as their loading increases. This could be explained, in part, by the polydispersity of the DOM solutions and competition among DOM components. With increasing DOM to sorbent ratios, loading increases as a greater fraction of smaller, more adsorbable components populate the sorbent surface and pore volume; these smaller components could penetrate more deeply into the pore structure. Alternatively, it is possible that, with increased loadings, surface and pore concentrations become high enough to cause adsorbed DOM molecules to change their configuration, becoming more compact and better able to penetrate more deeply into the carbon pore structure (35).

Another possibility is that the surface area reduced by DOM pore blockage is comprised mostly of surfaces accessible to TCE but not DOM. As DOM adsorbs in the smallest pores they can access, surface area in smaller pores (accessible to TCE) will decrease at a faster rate than the total surface area. Therefore, as total surface area is reduced, the surface area accessible to TCE exclusively would become a smaller fraction of the total, thus shifting  $\theta$  to smaller values. Under this hypothesis, the dependence of  $\theta$  on DOM loading should be related to changes in the pore size distribution after preloading, and changes in micropore volume should show a greater dependency on DOM loading than changes in total pore volume.

Nitrogen gas adsorption data measured for as-received and preloaded carbons was further analyzed using DFT to characterize changes in pore volume distributions as a result of DOM preloading. The DFT software used to calculate pore volume distributions was included with the Quantachrome Autosorb 1-C instrument. The DFT model considers sorbate–sorbate and sorbate–sorbent intermolecular forces to predict pore-filling pressures and molar volumes for a discreet number of pore sizes using the local mean-field molar density





**FIGURE 9.** Effect of <1 kDa TMK NOM loading on total pore volume (diamonds) and pore volume in pores <1.25 nm (squares) for preloaded carbon  $V_{\text{PRELOAD}}$ , relative to that of as-received carbon,  $V_{\text{AS-RECEIVED}}$ , as determined from density functional theory. Also shown (circles) is the effect of <1 kDa NOM fraction loading on correlated (Figure 7) values of the fraction of sorbent surface area,  $\theta$ , on which TCE adsorbs without competition from NOM.

approximation. A search for the distribution of pore sizes whose aggregate uptake matches the overall measured isotherm data is performed using a non-negative least squares error minimization routine.

For purposes of this analysis, it was assumed that DOM could not access pores having widths smaller than 1.25 nm. This estimate was based in part on data reported by Aiken and Malcolm (12) for the radii of gyration (measured using small-angle X-ray scattering) and molecular weight (measured by vapor pressure osmometry) of fulvic acids from five different natural water sources. The average radius of gyration of fulvic acids having molecular weights ranging from 594 to 829 was 0.68 nm. Because the radius of gyration is the radius at which the entire mass of the molecule would be located such that the moment of inertia would be the same as the actual mass distribution, actual molecular dimensions are likely to be somewhat larger. In addition, steric hindrance effects may play a role; therefore, it seems unlikely that a significant fraction of the DOM could access pores having widths smaller than 1.25 nm. In addition, volume in pores of this size was measured with good precision using a low-pressure limit of  $p/p_0 = 10^{-5}$ ; multiple analysis ( $N = 8$ ) of as-received TOG carbon resulted in a coefficient of variation of 3.2%.

The effect of <1 kDa TMK DOM loading on total pore volume and pore volume in pores having a width <1.25 nm, relative to that of as-received carbon, is shown in Figure 9. The volume in micropores <1.25 nm exhibits a significantly greater dependence on DOM loading than total pore volume. This result was also observed for the two other waters and supports the hypothesis that DOM loading reduces surface area accessible only to TCE to a greater extent than total surface area. Therefore, we conclude that pore blockage by DOM likely contributes to shifts in the value of  $\theta$  to smaller values with increased DOM loading; however, further work is needed to clarify the role of DOM polydispersity.

Advantages of the proposed model include (i) the reactive low molecular weight (<1 kDa) DOM fraction is a narrowly defined, identifiable component of the whole DOM mixture, which can be isolated and characterized in terms of its adsorptive character; and (ii) the model requires only one fitting parameter, which has physical meaning and is consistent with previous interpretations of DOM preloading phenomena. For these reasons, the model may be applied to accurately predict competitive adsorption over a wide range of preloading conditions. A potential disadvantage of the modeling approach is the significant experimental data

required. However, the remarkably similar preloading behavior of the <1 kDa fraction of the three different surface waters studied suggests that this approach may, with further verification, be used to develop a more general relationship that could then be applied to a wide range of natural surface water DOM using an abridged experimental protocol. Application of the MIAST approach to describe or predict TCE sorption in fixed-bed reactors would require knowledge of the loading of low molecular weight DOM components as a function of time and position in the bed. In addition, the effects of DOM preloading on TCE kinetics and how these effects change with DOM loading must be included, likely through a time-dependent intraparticle diffusion parameter (e.g., refs 5, 23, and 36). Therefore, further research is required to develop a comprehensive dynamic model.

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## Supporting Information Available

The full model formulation, isotherm parameters used in the modeling, and several figures showing MIAST predictions for the three surface waters studies over a range of DOM loadings. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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